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Electron Spin Resonance Studies of Anion Radicals of Benzoylsilanes

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ESR studies of anion radicals of seven substituted benzoylsilanes were investigated. ESR data of these anion radicals are discussed in comparison with those of aryl alkyl ketones. ESR spectra of secondary product derived from the anion radical of benzoylsilanes were also examined.

Metalloidal ketones have been of considerable interest as homologs of ketones; in this connection, their unusual chemical and spectroscopic properties have been compared with those of the common ketones.[1] The large bathochromic shifts observed in the electronic spectra of metalloidal ketones recently received attention.[2] Several quantitative theories have been presented to account for these shifts in lower energies.[3]

A variety of physical techniques have been employed in order to clarify the electronic spectra of metalloidal ketones. Electron spin resonance (ESR) is potentially useful to study this problem. An examination of the ESR spectra of anion radicals of benzoylsilanes gives quantitative information which is concerned with the unpaired electron occupying the π^* level.[3a]

Now we describe the ESR spectra of anion radicals of seven substituted benzoylsilanes. The ESR spectra of the secondary derived product derived from the anion radicals of benzoylsilanes are also reported.

Results and Discussion

ESR Spectra of Anion Radicals. Substituted benzoylsilanes (**1**) were reduced with potassium metal in 1,2-dimethoxyethane (DME) at −80 °C. These conditions were chosen so as to prevent any formation of secondary anion radicals derived from the anion radicals of **1**. The ESR spectra of the anion radicals of **1** are shown in Figs. 1—5. The *g* factors and hyperfine splitting constants (hfsc), determined by computer simulation, of anion radicals of **1** are summarized in Table 1 together with those of certain reported benzoylsilanes and two alkyl aryl ketones (**2**).

The ESR spectrum of an anion radical of benzoyltrimethylsilane (**1a**) obtained by potassium reduction in DME at −80 °C comprised about 15 lines, due to ring protons having g=2.0039. The experimental spectrum of the anion radical of **1a** was reproduced by computer simulation with the listed hfsc's. The ESR spectrum of the anion radical of **1a** observed in this study coincides exactly with that reported by Bock and co-workers.[4]

Each line splits further into a multiplet due to 9 equiv methyl protons (a_{SiMe}=0.14 G (1G=10^{-4} T)).

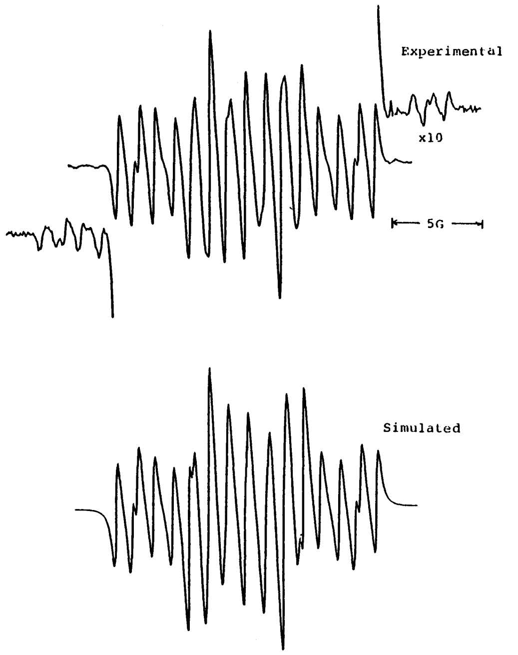


Fig. 1. ESR spectrum of anion radical of benzoylphenyldimethylsilane (**1b**) at −80 °C.

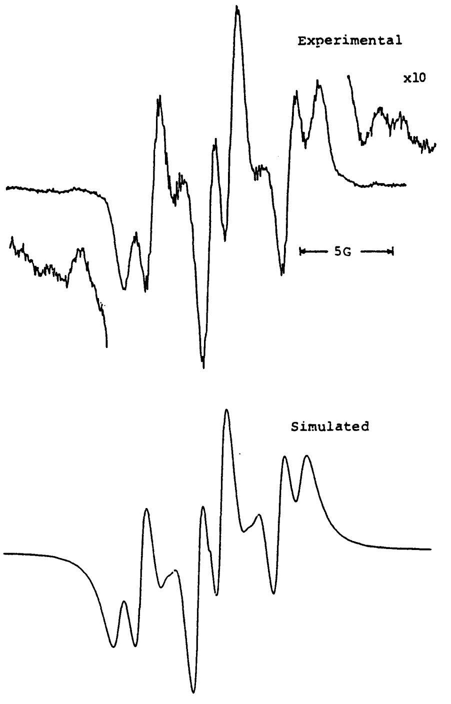


Fig. 2. ESR spectrum of anion radical of *p*-methoxylbenzoyltrimethylsilane (**1d**) at −80 °C.

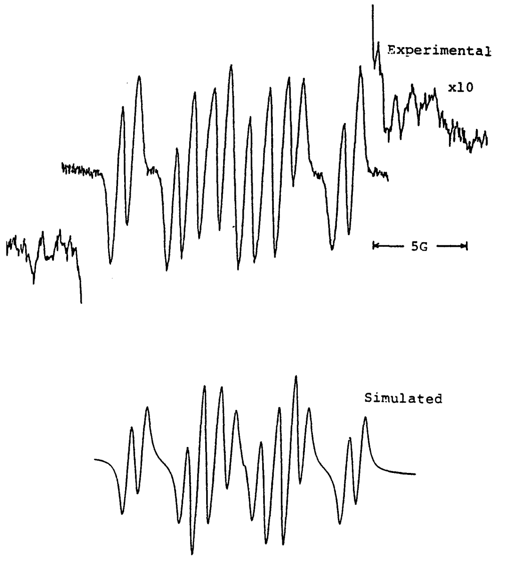


Fig. 3. ESR spectrum of anion radical of *m*-methoxylbenzoyltrimethylsilane (**1e**) at −80 °C.

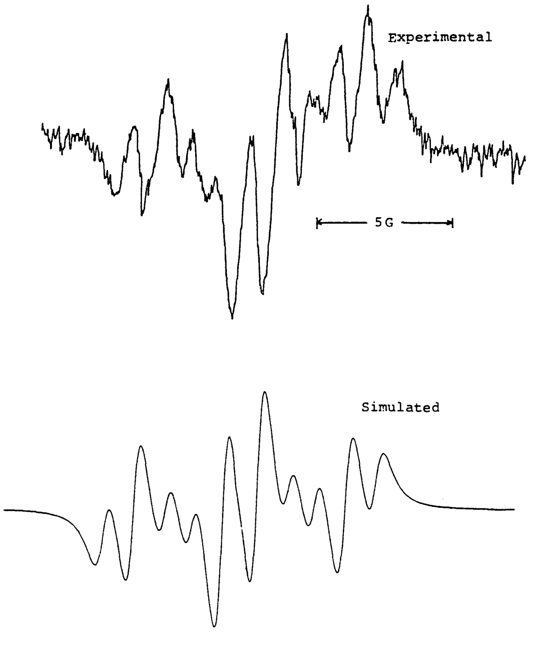


Fig. 4. ESR spectrum of anion radical of *p*-*t*-butylbenzoyltrimethylsilane (**1f**) at −80 °C.

Under higher gain, the ^{29}Si splitting (natural abundance=4.7%, $I=1/2$) of the anion radical of **1a** ($a_{\mathrm{Si}}=8.86$ G) was detected. The fact that the hyperfine coupling constants of two-protons are not equivalent indicates a restricted rotation of the phenyl group about the carbon-carbon bond.

The ESR spectrum of an anion radical of benzoyldimethylphenylsilane (**1b**), shown in Fig. 1, was interpreted in the same manner as described for **1a**. The ESR spectrum was reproduced by computer simulation with the hfsc's listed in Table 1. None of the hfsc's of both ortho- and meta-protons are equivalent.

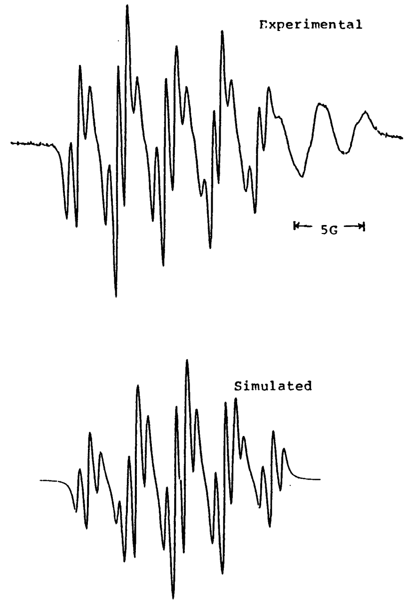


Fig. 5. ESR spectrum of anion radical of *p*-nitrobenzoyltrimethylsilane (**1g**) at −80 °C.

This fact also indicates a restricted rotation of the phenyl ring. Attempts to determine the rotational barrier by studying the temperature dependence of the ESR spectrum of the anion radical of **1b** were unsuccesful, since the spectrum was essentially unchanged over a temperature range between 0 and −80 °C. Upon warming above 0 °C, the new spectra of certain species, derived from an anion radical of **1b**, gradually appeared. The secondary ESR spectrum will be discussed later.

The ESR spectrum of an anion radical of *p*-methoxylbenzoyltrimethylsilane (**1d**) in DME at −80 °C is shown in Fig. 2. About 8 lines due to ring protons, and $g=2.0040$, were observed. Under higher gain, ^{29}Si splitting of the anion radical of **1d** ($a_{\mathrm{Si}}=9.53$ G) was detected. The coupling constants of two nonequivalent meta-protons could be determined by computer simulation.

The ESR spectra of anion radicals of *m*-methoxylbenzoyltrimethylsilane (**1e**) ($g=2.0042$) and *p*-*t*-butylbenzoyltrimethylsilane (**1f**) ($g=2.0040$) are shown in Figs. 3 and 4, respectively. The coupling constants of the anion radical of **1e**, shown in Table 1, were determined by computer simulation while taking the ESR data of the related silyl ketyls into consideration. The ESR spectrum of the anion radical of **1f** exhibits an essentially similar pattern to that of the anion radical of **1d**. The ESR spectra of **1e** and **1f** were also reproduced by computer simulation with the hfsc's listed in Table 1. Some of the line intensities of an anion radical of **1f** were not satisfactorily reproduced by computer simulation.

The ESR spectrum of an anion radical of *p*-nitrobenzoyltrimethylsilane (**1g**) ($g=2.0051$) and its computer simulation are shown in Fig. 5. At low field

Table 1. The *g* Factors and Hyperfine Coupling Constants of Anion Radicals of Benzoylsilanes and Aryl Ketones

Anion radical	*g* value	h.f.s. c/G				Reference
$R\text{-}C_6H_4\text{-}\dot{C}(O^-)\text{-}MR'_3$		$a_{o\text{-H}}$	$a_{m\text{-H}}$	$a_{p\text{-H}}$	others	
M=Si						
R=H, R'_3=Me_3 (**1a**)	2.0039	4.20(1H), 3.17(1H)	1.03(2H),	5.25(1H),	a_{SiMe} 0.14 a_{Si} 8.86	This work
		4.28(1H), 3.15(1H)	1.02(2H),	5.25(1H),	a_{SiMe} 0.13	4
R=H, R'_3=$PhMe_2$ (**1b**)	2.0040	4.20(1H), 3.24(1H),	1.27(1H), 0.92(1H)	5.23(1H),	a_{Si} 8.67	This work
R=H, R'_3=Ph_3 (**1c**)	2.0040	3.97(1H), 3.09(1H),	1.18(1H), 0.88(1H)	4.86(1H),	a_{Si} 8.56	6
R=*p*-OMe, R'_3=Me_3 (**1d**)	2.0040	4.60(1H), 3.22(1H),	1.28(1H), 1.22(1H)		a_{SiMe} 0.15 a_{Si} 9.53	This work
R=*m*-OMe, R'_3=Me_3 (**1e**)	2.0042	4.01(1H), 3.22(1H)	0.80(1H),	4.98(1H)	a_{Si} 9.0	This work
R=*t*-Bu, R'_3=Me_3 (**1f**)	2.0040	4.34(1H), 3.18(1H)	1.12(2H)			This work
R=*p*-NO_2, R'_3=Me_3 (**1g**)	2.0051	0.76(2H),	3.36(1H) 2.84(1H)		a_N 3.40	This work
M=C						
R=H, R'_3=Me_3 (**2a**)	2.0037	3.67(2H),	0.90(1H), 1.57(1H)	6.67(1H)		13
R=H, R'_3=Ph_3 (**2b**)		3.69(2H),	0.98(2H),	5.78(1H)		5

various contaminant signals appeared as the result of another signals. The assignment of the coupling constants of ortho and meta-protons was determined while taking those of the anion radical of *p*-nitroacetophenone into consideration.[5)]

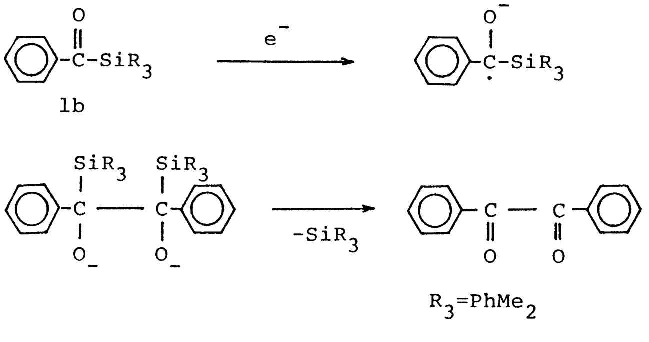
Three ESR spectra of anion radicals of benzoylgermanes, $PhCOGeR_3$ (R_3=Me_3, **3a**; R_3=$PhMe_2$, **3b**; R_3=Ph_3, **3c**) were also examined. These spectra all exhibit similar patterns (**3a**; g=2.0032, $a_{o\text{-H}}$=4.63, 3.45 G, $a_{m\text{-H}}$=1.32, 0.92 G, $a_{p\text{-H}}$=5.65 G. **3b**; g=2.0032, $a_{o\text{-H}}$=4.32, 3.38 G, $a_{m\text{-H}}$=1.22, 0.90 G, $a_{p\text{-H}}$=5.52 G. **3c**; g=2.0030, $a_{o\text{-H}}$=4.24, 3.34 G, $a_{m\text{-H}}$=1.24, 0.88 G, $a_{p\text{-H}}$=5.54 G). It may well be that the ESR spectra obtained can be assigned to the germyl radical adducts of benzoylgermanes, $[Ph\dot{C}(OGeR_3)GeR_3]$.[6)]

As shown in Table 1, the *g* factors of the anion radicals of **1** are larger than those of the carbon analogs **2**. It has been pointed out that the larger *g* factors of anion radicals of silylketyls reflect the lower energy of the carbonyl π^* orbital in these radical anions.[3b,7)] The interaction of silicon's d orbital with the π^* orbital leads to a lowering of the energy of this orbital. Electron delocalization of $Si \leftarrow C_\pi$ in the radical anions of **1** can be shown form the ^{29}Si coupling constants.

Secondary Anion Radicals. When the anion radical of **1b** was allowed to warm to above 0 °C, a new ESR spectra of the secondary anion radical arising from the original radical of **1b** gradually appeared. The new anion radical was found to be a 1,4-bis(phenyldimethylsilyl)benzene anion radical ($a_{o,\,m\text{-H}}$=2.54 G and a_{SiMe}=0.31 G). The ESR the spectrum of the 1,4-bis(phenyldimethylsilyl)benzene anion radical was confirmed by computer simulation and by a comparison with an authentic anion radical. Then, the 1,4-bis(phenyldimethylsilyl)benzene anion radical changed to an unidentified paramagnetic species with time. The formation of 1,4-bis(phenyldimethylsilyl)benzene is not easy to explain. In general, the formation of a trace of benzene is known in reactions of phenyl-substituted silyl compounds with alkali metals.[8)] Silyl anions have been reported to react with benzene to give 1,4-bis(phenyldimethylsilyl)benzene.[9)]

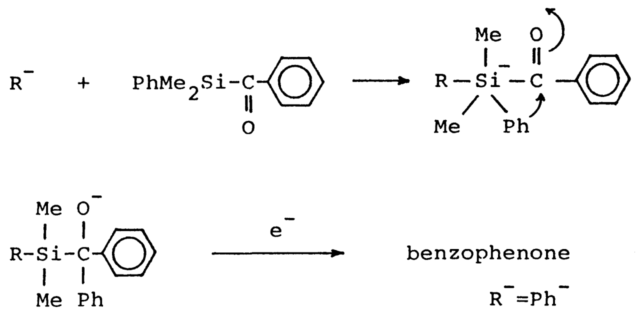
The radical anion of **1b** when warmed to 20 °C changed to either benzophenone ketyl ($a_{o\text{-H}}$=2.60 G, $a_{m\text{-H}}$=0.87 G, and $a_{p\text{-H}}$=3.45 G) or benzil anion radical ($a_{o\text{-H}}$=1.00 G, $a_{m\text{-H}}$=0.36 G, and $a_{p\text{-H}}$=1.10 G), the change being dependent upon the amounts of **1b** and potassium metal used. Benzophenone ketyl and benzil anion radical are stable under these conditions.

The formation of benzil from **1b** can be interpreted by a mechanism involving a coupling of the initially formed radical anion of **1b**, followed by an elimination of the phenyldimethylsilyl anion, as outlined below.



There may be an alternative mechanism which involves a dimerization of the benzoyl radical, first formed by an elimination of the silyl anion radical of **1b**.

The formation of benzophenone from **1b** might be explained by the work of Brook and co-workers.[10] Thus, an attack by a nucleophile must occur on the silicon atom of **1b**, followed by a 1,2-migration of a phenyl group to the adjacent carbonyl group, as shown below. The α-silyl alkoxide formed may undergo homolysis of a silicon-carbon bond to give benzophenone. An analogous mechansim for the formation of benzil and benzophenone has been postulated by Arberti and co-workers.[6]



Experimental

ESR Measurements. All the ESR spectra were obtained using a Varian E-9 ESR spectrometer. The field sweep of the spectrometer was calibrated with an aqueous solution of Fremy's salt (a_N=13.07 G). The g factors were determined by reference to that of Fremy's salt (g=2.0055) using a dual cavity.

Materials. Benzoyltrimethylsilane,[3a] benzoylphenyldimethylsilane,[3a] *p*-methoxybenzoyltrimethylsilane,[3a] *m*-methoxybenzoyltrimethylsilane,[3a] *p*-nitrobenzoyltrimethylsilane,[3a] benzoyltrimethylgermane,[3a] benzoylphenyldimethylgermane,[11] and benzoyltriphenylgermane[12] were prepared according to the cited literatures. DME was dried over sodium- potassium alloy.

ESR Studies of Anion Radicals of Benzoylsilanes. The ESR samples were prepared in 3-mm Pyrex sample tubes which were sealed to an 8-mm tube having a side arm and an "O" ring fitting for attaching the sample preparation tube to the vacuum line. The desired potassium metal was placed in the side arm, a very small amount of the desired benzoylsilane was placed in the sample tube, and the entire apparatus was attached to a vacuum line. The sample was degassed and DME was transferred from the reservoir while filling the sample tube to a height of about 70—100 mm. The potassium was then distilled from the side arm into the upper portion of the Pyrex sample tube, and the tube was sealed off. The samples were kept frozen in liquid nitrogen until used. To develop the radical anion of benzoylsilane, the contents of the sample tube were allowed to warm to slightly above the melting point; the tube was then inverted in order to bring the sample into contact with the mirror, at which time the sample tube was immediately inserted into the variable-temperature probe of the spectrometer, which was cooled to about −80 °C.

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